NASA TT F-11,379

SPECTROPHOTOMETRIC DETERMINATION OF MINUTE QUANTITIES OF IODIDE AND BROMIDE

Tadao Okutani

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

Nippon Kagaku Zasshi, Vol. 88, No. 7, pp. 737-741, 1967.

FACILITY FORM 602

N68-16094 (ACCESSION NUMBER) (THRU) 1

(PAGES) (CODE)

(NASA CR OR TMX OR AD NUMBER) 06 (CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 NOVEMBER 1967

SPECTROPHOTOMETRIC DETERMINATION OF MINUTE QUANTITIES OF IODIDE AND BROMIDE

Tadao Okutani*

ABSTRACT. The determination of minute quantities of iodide and bromide, when iodide,bromide and chloride are present.

Studies were made on the determination of minute quantities of iodide and /737** bromide when iodide, bromide and chloride are present.

When a fixed amount of mercury reagent A, ($Hg(NO_3)_2$-KI), and an ethanol solution of diphenylcarbazone are added to the sample solution, iodide ions react with the mercury reagent. The excess mercury reagent reacts with diphenylcarbazone and forms a purplish-red complex which is soluble in benzene. By measuring the absorbance of the benzene layer at 562 mμ, 0.1~3.0 ppm iodine can be quantitatively determined, when 100 ppm chlorine and 2 ppm bromine are present.

When chloride and iodide ions are present, bromide ions cannot be quantitatively determined with this method. In this case, the following method is used: Bromide ions are oxidized to bromine with potassium permanganate, which is extracted with tetrachloromethane. Add mercury reagent B, ($Hg(NO_3)_2$-KI-$Hg(SCN)_2$), nitric acid, diphenylcarbazone solution and shake. Bromine is determined by measuring the absorbance of the tetrachloroethane layer at 560 mμ.

With this method, 0.1~2.5 ppm bromine can be accurately determined even when 1000 ppm chloride and 50 ppm iodide ions are present.

1. Introduction

For the colorimetric analyses of minute quantities of iodine, and bromine, there are many good methods, such as: mercuric thiocyanate method (Ref. 1), fluoroscein method (Ref. 2), mercury-diphenylcarbazone-benzene extraction method (Ref. 3), and a catalytic method (Ref. 4-6).

With the catalytic method, 0.001~10 ppm iodide, and 0.003~0.5 ppm bromide ions can be quantitatively determined when iodide, bromide, and chloride ions are present. The determinations of iodide, and bromide ions, however, cannot be conducted simply with other methods when all of these ions are present.

Iwasaki (Ref. 7, 8), et. al., report on a quantitative method when such ions are present. Bromide ions are first oxidized to bromine with potassium permanganate in a sulfuric acid solution. Iodide ions are then oxidized to

* Tadao Okutani, Nippon University, Department of Science and Engineering, Surugadai Kanda, Chiyodaku, Tokyo.

** Note: Numbers in the margin indicate pagination in original foreign text.

iodine with hydrogen peroxide solution. They are each extracted with tetrachloromethane, and 1~5 ppm bormide, and 1~60 ppm iodide ions are colorimetrically determined with the mercuric thiocyanate method.

The author has previously reported on colorimetric methods for the indirect analyses of minute quantities of chloride (Ref. 9), thiosulfate (Ref. 10), sulfide (Ref. 11), cyanate (Ref. 12), and sulfurous ions (Ref. 13), by extracting the complex formed by adding a mercury salt and diphenylcarbazone reagent.

Although a colorimetric method for the analyses of minute quantities of iodide, and bromide ions, based on such a theory was reported by Tomonari (Ref. 3), the method of determination has not been examined when iodide, bromide, and chloride ions are present. The author conducted a study for the purpose of analyzing for iodide and bromide ions when they are both present, using the mercury saltdiphenylcarbazon-benzene extraction method. Following the previously reported procedure (Ref. 10-13), 0.1~3.0 ppm iodide ions can be quantitatively determined, even when 100 ppm of chloride, and 2 ppm of bromide ions are present. Nevertheless, since bromide ions cannot be determined with this method when minute quantities of chloride and iodide ions are present, they were separated as follows: when bromide ions are oxidized in a proper concentration of sulfuric acid with potassium permanganate, they are quantitatively oxidized to bromine even when they are present in a minute quantity, while chloride ions are not oxidized even when they are present in large amounts. Iodide ions are oxidized to the iodate ions (Ref. 7). The separated bromine is extracted with tetrachlormethane, discolored by adding mercury salt, and diphenylcarbazone and the absorbance of the tetrachloromethane layer is measured at 560 mμ. With this method, 0.1~2.5 ppm bormide ions can be accurately determined, even when 1000 ppm chloride, and 50 ppm iodide ions are present. /738

The concentration range is between that of the previously reported catalytic method, and the mercuric thiocyanate method. The method is applicable for the quantitative determination of iodide, and bromide ions in natural water.

2. Reagents and Apparatus

2.1 The Standard Solutions of Iodide and Bromide Ions

Approximately 0.1 mol/l solution is prepared by dissolving special grade potassium iodide or bromide in water. The solution was standardized by the Volhard method and stored in a cool place in a brown bottle. The solution was then diluted in 10 ppm water.

2.2 Potassium Permanganate Solution (0.02 m/l)

Special grade potassium permanganate was used to make the standard solution by following the standard procedure (slightly more concentrated than 0.02 mol/l). Sodium oxalate was used to determine the concentration. It was diluted to 0.02 mol/l with water, and stored in a brown bottle.

2.3 Mercuric (II) Thiocyanate Solution

1.50 g of mercuric (II) thiocyanate prepared according to the method by

Utsumi (Ref. 14) was dissolved in 500 cc methanol, and stored in a brown bottle.

2.4 Mixed Solutions A, and B

A: Mix equal volumes of 5×10^{-4} mol/l mercuric (II) nitrate, and 5×10^{-4} mol/l potassium iodide.

B: Add 2.5 ml of the mercuric (II) thiocyanate solution to 100 ml of the mixed A solution and store both in brown bottles.

2.5 Sulfuric Acid

Special grade sulfuric acid was diluted to 18 N.

2.6 Tetrachloromethane

Place special grade tetrachloromethane into a large separatory funnel, and shake with approximately 1/5 volume of concentrated sulfuric acid. After separating, wash again with concentrated sulfuric acid (if sulfuric acid discolors, repeat the process). Then wash by shaking with 1/3 volume of water followed by approximately 1/3 volume of 5% sodium hydroxide. After separating, wash with water, distill and collect the fraction with bp 77°C.The tetrachloromethane used was washed with water and re-used after recovering by the above method.

2.7 Separatory Funnel

50 ml volume, white and brown colored separatory funnels were used.

2.8 Shaker

A KM type, Universal Shaker U-S by Iwaki K.K.was used. The previously reported reagents and apparatus were used (Ref. 9-13). Special grade reagents were used.

3. Experimental Results and Discussion

3.1 Procedure and the Standard Curves of Iodide and Bromide Ions

Place 10 ml of the neutral solution containing iodide and bromide ions in a brown separatory funnel, and add 1 ml, 0.05 N nitric acid, and 1 ml of mixed solution A. Then add 10 ml benzene, 1 ml diphenylcarbazone solution (0.05 g diphenylcarbazone is dissolved in 100 ml ethanol, which will be abbreviated as DC solution), and shake for 1 minute. Allow to stand for 1~2 minutes for the two layers to separate. Separate the purple-red colored benzene layer, and measure the absorbance at 562 mμ in a 10 mm cell. The concentrations of the iodide, and the bromide ions are determined from the standard curves.

Standard curves (1) and (3) in Figure 1 were obtained at 21°C liquid temperature, using the standard solutions which contain known concentrations of iodide and bromide ions. When used under the same conditions, the reproducibility is good, and 0.1 ~ 3.0 ppm iodide, and 0.1~2.0 ppm bromide ions can be rapidly and accurately determined.

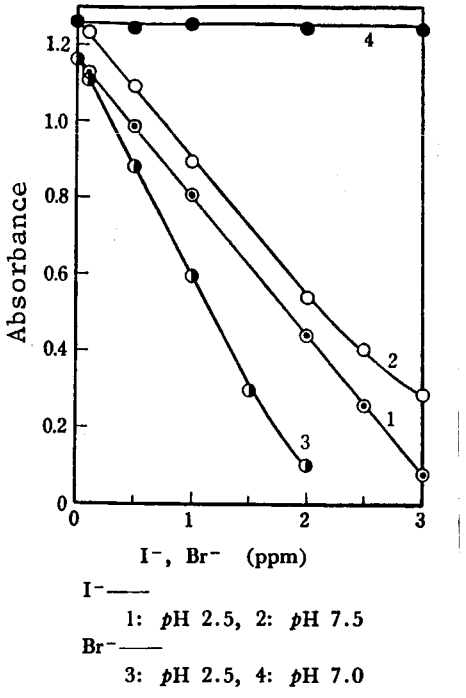

Figure 1. Standard Curves of Iodide and Chloride Ions by Procedure 3.1 (Benzene Extraction).

The discussion of experimental conditions, such as the effects of the concentration and the temperature will be omitted, since it was previously reported (Ref. 9, 10).

It was reported previously (Ref. 10, 11) that when thiosulfate and sulfide ions are quantitatively determined at pH 7, 100 ppm chloride ions do not interfere. Since minute quantities of chloride ions interfere with the previously described method (pH 2.5), a 1 ml phosphate buffer solution (pH 7) was added in place of the 0.05 N nitric acid. Standard curves (2) and (4) in Figure 1 were obtained by this procedure. As indicated in Figure 1, although iodide ions can be determined with approximately the same sensitivity at pH 2.5 or 7, the absorbance of bromide ions does not change at pH 7 even when the concentration is increased to 3 ppm. Hence, analyses were conducted with larger concentrations of bromide ions and the results are shown in Table I. The absorbance decreases as the bromide concentration increases; it was, however, almost negligible up to 2 ppm. Hence, bromide ions cannot be determined by this method. A similar experiment was carried out with chloride ions, which showed that absorbance does not change even when 100 ppm is present. Hence, working at pH 7, up to 100 ppm chloride or 2 ppm bromide ions do not interfere, which permits the quantitative determination of minute amounts of iodide ions.

TABLE I. THE EFFECT OF BROMIDE ION (LIQUID TEMPERATURE 21°C) /739

Br^- (ppm)	Absorbance	Br^- (ppm)	Absorbance
--	1.25_1	10	1.20_0
--	1.25_9	50	0.97_4
2	1.24_4	100	0.83_5
5	1.22_9		

3.2 Determination of Bromide Ions When Iodide and Chloride Ions Are Present

Bromide ions cannot be determined easily when chloride and iodide ions are present. In such cases, the diffusion method (Ref. 15) or the method by which bromide is oxidized to bromine and extracted with chloroform or tetrachloromethane (Ref. 7, 16), are used.

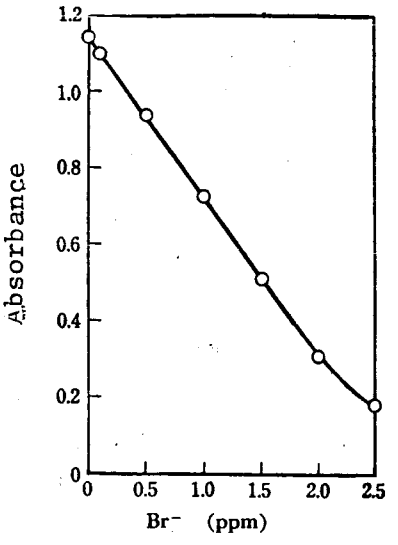

Figure 2. Standard Curve of Bromide Ions by Procedure 3.2.1.

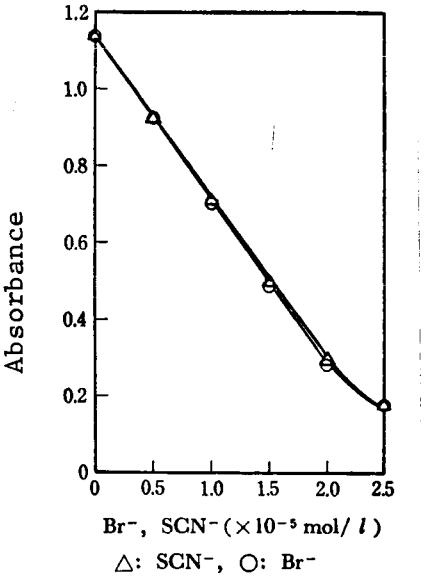

Figure 3. Standard Curves of Bromide and Thiocyanate Ions (Tetrachloromethane Extraction).

Iwasaki, et. al., oxidized bromide ions to bromine with sulfuric acid and potassium permanganate, extracted with tetrachloromethane and determined 1～50 ppm bromide ions by the mercuric thiocyanate method.

The author examined the method in order to carry out the analyses using the mercuric-diphenylcarbazone method after separating it with this method (Ref. 7).

3.2.1 Procedure and Calibration

Place 10 ml of sample solution containing bromide in a separatory funnel and add 0.3 ml 18 N sulfuric acid, 0.7 ml 0.02 mol/l potassium permanganate solution and allow it to stand for 10 minutes. Extract twice with 5 ml purified tetrachloromethane (shake for 1～2 minutes and separate after 1～2 minutes*), and transfer the tetrachloromethane into another separatory funnel. Wash once, by adding 5 ml 1 N sulfuric acid and transfer the separated tetrachloromethane into a brown separatory funnel.

* Shaking time of more than 1 minute is enough. When the coexisting chloride and iodide ions are present in large quantities, the formation of manganese dioxide increases, which prolongs the separation time of the aqueous, and tetrachloromethane layers.

Add 1 ml, 0.05 N nitric acid, 1 ml mixed solution B, 1 ml DC solution and shake for 5 minutes. After allowing it to stand for 1~2 minutes, measure the absorbance at 560 mμ in a 10 mm cell. The concentration of the bromide ions is determined from the standard curve.

A standard curve shown in Figure 2 was obtained at 21°C liquid temperature using the standard solution. When the conditions are kept constant, the reproducibility is good and 0.1~2.5 ppm bromide ions can be determined accurately.

3.2.2 Extraction Solvent

Benzene is not suitable, since the extractability of bromine in benzene is very small. Tetrachloromethane, chloroform or carbon disulfide are commonly used. Tetrachloromethane was used, since it was found to extract the complex formed by the mercuric salt and DC solution, efficiently. Since the absorption maxima of the complex in tetrachloromethane was at 560 mμ, all absorption measurements were carried out at this wavelength.

3.2.3 Mixed Solution

Since good results were not obtained using mixed solution A and following procedure 3.2.1, it was decided to use the solution containing mercuric thiocyanate (mixed solution B). Figure 3 shows the calibration curves obtained at 0 2.5×10^{-5} mol/l bromide and thiocyanate concentration range using 1 ml of mixed solution B, and 10 ml of tetrachloromethane, and following procedure 3.1 (pH 2.5). Both curves showed good agreement; we found that the method is applicable for thiocyanate ions as well as for bromide ions.

Bromide and mercuric thiocyanate ions appear to react according to equation (1) (Ref. 7). The author, therefore, derived a method whereby bromine is indirectly extracted into the tetrachloromethane layer; bromide ions react with mercuric thiocyanate, and the thiocyanate ions formed (equivalent to bromide ions present) are treated according to 3.1.

$$6\,Br_2 + 7\,Hg(SCN)_2 + 8\,H_2O = 6\,HgBr_2 + Hg(CN)_2 + 2\,SO_4^{2-} + 12\,SCN^- + 16\,H^+ \quad (1)$$

Upon examining the amount of mercuric (II) thiocyanate in 1 ml of mixed solution B, the minimum quantity of bromide ions analyzable was found to be 60 μg when analyzing for less than 2.5 ppm bromide ions. Hence, in this method, 1 ml of the solution prepared by adding 2.5 ml of the mercuric (II) thiocyanate solution to the mixed solution A (1.5 g/500 ml), was used. Based on these findings, procedure 3.3.1 was followed when chloride and iodide ions are present.

3.2.4 The Effect of Shaking Time

Solutions containing 2.0 and 0.5 ppm bromide ions were treated according to 3.2.1. DC solution was added and the shaking time was varied. The results are shown in Figure 4.

Although 1 minute shaking was sufficient for the solution containing 2 ppm bormide ions, more than 3 minutes of shaking for the solution containing 0.5 ppm

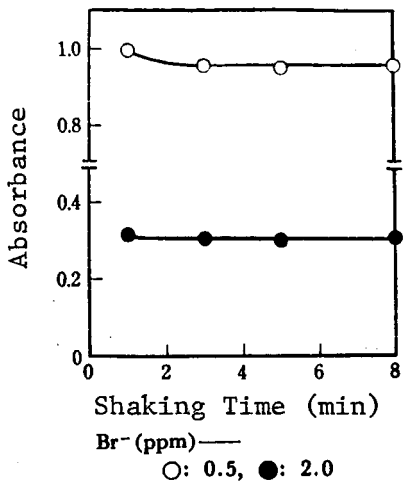

Figure 4. The Effect of Shaking Time.

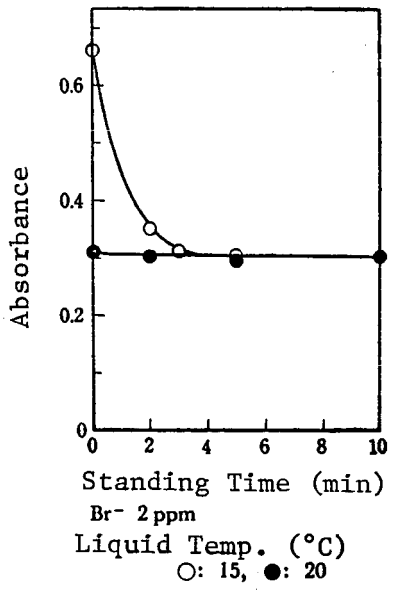

Figure 5. The Effect of Temperature, and Standing Time.

was required before a constant absorbance was obtained. From such findings it appears that it requires some time for the bromine in the tetrachloromethane layer to react with the mercuric (II) thiocyanate in the aqueous layer (i.e., equation [1]) when the concentration of bromide ions is small, although the extraction of the purple-red complex into the tetrachloromethane layer is extremely fast. The shaking time, therefore, was set at 5 minutes.

3.2.5 Examination of the Oxidation Conditions

Since the concentration and amount of sulfuric acid and potassium permanganate which must be used to oxidize bromide to bromine have been extensively studied (Ref. 7), we decided to add 0.3 ml, 18 N sulfuric acid, and 0.7 ml, 0.02 mol/l potassium permanganate solution to a 10 ml neutral sample solution, which is considered to be the best procedure. Detailed studies were also conducted on the effects of temperature and the standing time (time allowed after the above reagents are added to the sample solution until the first extraction is carried out). The author, however, experimented with 2 ppm bromide ion concentration for the purpose of examining the oxidation condition at temperatures below 20°C. The results are shown in Figure 5. It takes 5 minutes at 15°C and 2 minutes at 20°C for the oxidation to bromine.

When iodide and chloride ions are present, though, iodide ions are oxidized to the iodate ions under this oxidation condition; at low temperatures some are oxidized only to free iodine. Hence, solutions containing appropriate quantities of iodide ions were oxidized under conditions indicated in Table II, and were analyzed according to 3.2.1. The results are shown in Table II. Although a minute quantity of free iodine is left with 5 minutes oxidation at 20°C, they are oxidized to the iodate ions with 10 minutes oxidation at 15 or 20°C, even when the concentration is 50 ppm.

TABLE II. THE EFFECT OF IODIDE IONS

Oxidation Condition			Absorbance	
Temperature (°C)	Standing Time (min)	I⁻(ppm)	No Br^-	Br^- 1 ppm
20	10	—	1.14_2	0.30_1
15	10	10	1.14_8	0.31_0
		30	1.15_4	0.30_5
		50	1.14_2	0.30_6
20	5	5	1.07_5	0.30_3
		10	1.04_5	0.30_1
		30	0.88_2	0.30_5
		50	0.53_4	0.46_7
20	10	10	1.13_6	0.29_5
		30	1.14_8	0.30_3
		50	1.14_2	0.29_8

Iwasaki, et. al., examined the effect of chloride ions, mostly when they are present in a large quantity, such as 10,000 ppm.In our case, if 1000 ppm chloride has no effect, then it does not affect the quantitative determinations of 0.1～2.5 ppm bromide ions in natural water. Since even the chloride ions are oxidized if the temperature is high under these oxidation conditions, sulfuric acid, and potassium permanganate solution were added to two solutions, one with 2 ppm bromide ions and one without bromide ions at 15°～30°C. The solutions were allowed to stand for a constant length of time, and analyzed following 3.2.1 in order to examine the effect of 1000 ppm chloride ion. The absorbances were constant, regardless of the presence of chloride ions, when the standing time was less than 20 minutes. From such findings, the temperaature of the solution was set to 15°～30°C, and the solutions were allowed to stand for 10 minutes after sulfuric acid and potassium permanganate solution were added. Under these conditions, bromide ions can be separated and quantitatively determined even when 50 ppm iodide, and 1000 ppm chloride ions are present.

3.2.6 Washing

When bromine is extracted in the presence of chloride ions, the chloride ion mixes into the tetrachloromethane layer. Since even 0.1 ppm chloride ion is detrimental at this stage,they must be removed completely. They are removed by washing the tetrachloromethane layer onee with 1 N sulfuric acid (Ref. 7). When the organic layer was washed according to such a procedure, a large amount of chloride ions showed hardly any effect.

The presence of minute quantities of potassium permanganate or manganese dioxide (IV) in the organic layer is also detrimental. They are, however, easily removed by washing once with sulfuric acid. The tetrachloromethane layer, therefore, is washed regardless of the presence of chloride ions.

3.2.7 The Effect of Coexisting Ions

Since the effect of coexisting ions pertaining to procedure 3.1 has been discussed (Ref. 9, 10), the examination here will be limited only to those which have great effects and to those which are likely to be contained in natural water. The results of the study on the effect of the coexisting ions on the quantitative analyses of bromide ions, when analyzed according to procedure 3.2.1, are shown in Table III. /741

Silver, thiocyanate and cyanate ions were found to be detrimental even when they are present in 1 ppm level. As shown in Table III, the effect of the other ions was relatively small.

TABLE III. EFFECT OF COEXISTING IONS (20°C)

Coexisting Ions		Absorbance	
Ions	ppm	No Br^-	Br^- 2 ppm
—	—	1.14_2	0.30_4
		1.14_8	0.30_1
Ca^{2+}	100	1.13_6	0.29_2
Mg^{2+}	100	1.15_4	0.30_7
Cu^{2+}	10	1.14_8	0.31_0
Fe^{2+}	10	1.15_4	0.31_1
Ag^+	1	1.15_1	0.55_2
$S_2O_3^{2-}$	10	1.13_6	0.30_7
SO_3^{2-}	10	1.14_2	0.30_8
S	10	1.13_6	0.31_0
SCN^-	1	1.14_8	0.52_2
	10	1.15_4	1.03_6
CN^-	1	1.15_4	0.74_4

4. Conclusion

The complex ions, formed by adding diphenylcarbazone solution to the mixed solution of mercuric (II) nitrate-potassium iodide, were extracted with benzene, and minute quantities of iodide ions (0.1~3.0 ppm) and bromide ions (0.1~2 ppm) which react indirectly with mercury ions were determined colorimetrically.

Conditions were established under which 2 ppm bromide or 100 ppm chloride ions do not interfere with the quantitative determination of iodide ions. Since bromide ions cannot be determined when minute quantities of iodide or chloride ions are present, the bromide ions were separated from the others by oxidizing to bromine which were extracted with tetrachloromethane and determined colorimetrically.

According to the established method, 0.1~2.5 ppm bromide ions can be accurately determined in the presence of 50 ppm iodide and 1000 ppm chloride ions without interference.

I thank Professor Satoshi Utsumi for his valuable advice and guidance.

REFERENCES

1. Utsumi, Satoshi. Nikka, 73, 889, 1952; 74, 32, 1953.
2. Pohl, F. A. Z. Anal. Chem., 149, 68, 1956.
3. Tomonari, Akihisa. Nikka, 83, 459, 1962.
4. Shiota, Katsu; Utsumi, Satoshi; Iwasaki, Iwaji. Nikka, 80, 752, 1959.
5. Utsumi, S. Nikka, 74, 298, 1953.
6. Utsumi, S., Shiota, K., Maibara, Hanshin, Iwasaki, I. Nikka, 85, 32, 1964.
7. Iwasaki, I., Utsumi, S., Tomonari, A., Morita, Ichiro, Shiota, K. Nikka, 80, 744, 1959.
8. Iwasaki, I., Utsumi, S., Tomonari, A. Nikka, 80, 749, 1959.
9. Utsumi, S., Okatani, T. Nikka, 85, 543, 1964.
10. Okutani, T., Utsumi, S., Shibata, Kenya, Iwasaki, I. Nikka, 86, 831, 1965.
11. Okutani, T., Utsumi, S. Nikka, 86, 1149, 1965.
12. Okutani, T., Utsumi, S. Nikka, 87, 444, 1966.
13. Okutani, T., Utsumi, S. Bull. Chem. Soc., 40, 1386, Japan, 1967.
14. Utsumi, S. Nikka, 73, 835, 1952.
15. Koga, Shojin. Nikka, 79, 1026, 1958.
16. Ishibashi, Masayoshi, Sahara, Ryotaro. Nikka, 61, 513, 1940.

Scientific Translation Service
4849 Tocaloma Lane
La Canada, California 91011

NASw-1496